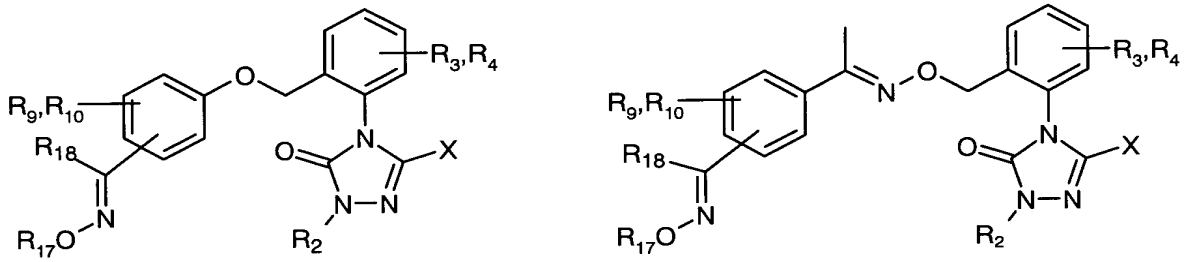
Unsaturated oxime ethers and the use thereof for control of harmful fungi and veterinary pests

The present invention relates to unsaturated oxime ethers, to intermediates for their preparation and to their use for controlling harmful fungi and animal pests.

Fungicidal oxime ether compounds are already known. WO 95/14009, WO 96/17851, WO 96/36229, WO 96/36615, WO 96/36616, WO 96/36633, WO 97/0612, WO 98/05652 and WO 98/23155, for example, describe strobilurins having triazolone pharmacophores, of the formula:



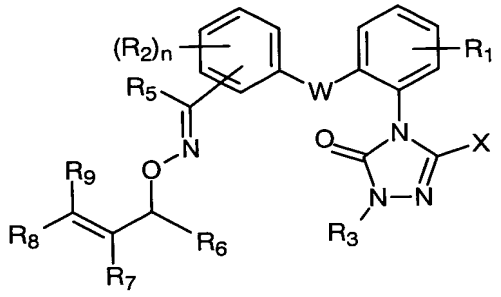
in which R_{17} and R_{18} are H, C_1-C_3-alkyl or phenyl.

Compounds having unsaturated oxime ether side-chains have already been disclosed in EP 386561A, EP 579124A, EP 585751A, EP 672347A, EP 673923A, WO 97/30032 and WO 97/33874.

It is an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum.

We have found that this object is achieved by compounds having a triazolone pharmacophore and an unsaturated oxime ether side-chain.

Accordingly, the present invention relates to unsaturated oxime ether compounds of the formula 1



1

where

W is $-OCH_2-$, $-C(R_{10})=N-O-CH_2-$ (where the CH_2 end is in each case attached to the phenyl group carrying the triazolone radical);

X is halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy;

R_1 is H, C_1-C_4-alkyl, halogen, nitro, CN, halo-C_1-C_4-alkyl, C_1-C_4-alkoxy;

R_2 is H, C_1-C_4-alkyl, halogen, nitro, CN, halo-C_1-C_4-alkyl, C_1-C_4-alkoxy;

n is 1 or 2;

R_3 is H, C_1-C_4-alkyl;

R_5 is H, C_1-C_4-alkyl, C_2-C_4-alkenyl;

R_6 is H, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_2-C_4-alkenyl, aryl;

R_7 is H, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_2-C_6-haloalkenyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, unsubstituted or substituted aryl;

R_8 is H, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_2-C_6-haloalkenyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, unsubstituted or substituted aryl, or

R_7 and R_8, together with the carbon atoms to which they are attached, form an unsaturated heterocycle having 5 or 6 ring atoms and one or two heteroatoms, independently of one another selected from nitrogen, oxygen and sulfur, which heterocycle may be substituted by one or two radicals which, independently of one another, are selected from the group consisting of C_1-C_4-alkyl, halogen, nitro, CN,

halo-C_1-C_4-alkyl, OH, C_1-C_4-alkoxy, unsubstituted or substituted aryl, C_2-C_4-alkenyl, halo-C_2-C_4-alkenyl, C_2-C_4-alkynyl, halo-C_2-C_4-alkynyl;

R_9 is H, halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_2-C_6-haloalkenyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, unsubstituted or substituted aryl;

R_{10} is H, halogen, C_1-C_4-alkyl.

The meanings listed above are collective terms for individual enumerations of the individual group members. All hydrocarbon chains can be straight-chain or branched. Halogenated substituents preferably carry 1 to 5 identical or different halogen atoms.

Specific meanings are, for example:

- halogen: fluorine, chlorine, bromine, iodine, preferably fluorine or chlorine;

- C_1-C_4-alkyl: methyl, ethyl, n-propyl, 1-methylethyl, n-butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, preferably methyl;

- C_1-C_6-alkyl: C_1-C_4-alkyl as mentioned above, and also n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl, preferably methyl, ethyl, n-propyl, 1-methylethyl, n-butyl or 1,1-dimethylethyl;

- C_2-C_6-alkenyl: ethenyl, prop-1-en-1-yl, prop-2-en-1-yl, 1-methylethenyl, n-buten-1-yl, n-buten-2-yl, n-buten-3-yl, 1-methylprop-1-en-1-yl, 2-methylprop-1-en-1-yl, 1-methylprop-2-en-1-yl, 2-methylprop-2-en-1-yl, n-penten-1-yl, n-penten-2-yl, n-penten-3-yl, n-penten-4-yl, 1-methylbut-1-en-1-yl, 2-methylbut-1-en-1-yl, 3-methylbut-1-en-1-yl, 1-methylbut-2-en-1-yl, 2-methylbut-2-en-1-yl, 3-methylbut-2-en-1-yl, 1-methylbut-3-en-1-yl, 2-methylbut-3-en-1-yl, 3-methylbut-3-en-1-yl, 1,1-dimethylprop-2-en-1-yl,

1,2-dimethylprop-1-en-1-yl, 1,2-dimethylprop-2-en-1-yl, 1-ethylprop-1-en-2-yl, 1-ethylprop-2-en-1-yl, n-hex-1-en-1-yl, n-hex-2-en-1-yl, n-hex-3-en-1-yl, n-hex-4-en-1-yl, n-hex-5-en-1-yl, 1-methylpent-1-en-1-yl, 2-methylpent-1-en-1-yl, 3-methylpent-1-en-1-yl, 4-methylpent-1-en-1-yl, 1-methylpent-2-en-1-yl, 2-methylpent-2-en-1-yl, 3-methylpent-2-en-1-yl, 4-methylpent-2-en-1-yl, 1-methylpent-3-en-1-yl, 2-methylpent-3-en-1-yl, 3-methylpent-3-en-1-yl, 4-methylpent-3-en-1-yl, 1-methylpent-4-en-1-yl, 2-methylpent-4-en-1-yl, 3-methylpent-4-en-1-yl, 4-methylpent-4-en-1-yl, 1,1-dimethylbut-2-en-1-yl, 1,1-dimethylbut-3-en-1-yl, 1,2-dimethylbut-1-en-1-yl, 1,2-dimethylbut-2-en-1-yl, 1,2-dimethylbut-3-en-1-yl, 1,3-dimethylbut-1-en-1-yl, 1,3-dimethylbut-2-en-1-yl, 1,3-dimethylbut-3-en-1-yl, 2,2-dimethylbut-3-en-1-yl, 2,3-dimethylbut-1-en-1-yl, 2,3-dimethylbut-2-en-1-yl, 2,3-dimethylbut-3-en-1-yl, 3,3-dimethylbut-1-en-1-yl, 3,3-dimethylbut-2-en-1-yl, 1-ethylbut-1-en-1-yl, 1-ethylbut-2-en-1-yl, 1-ethylbut-3-en-1-yl, 2-ethylbut-1-en-1-yl, 2-ethylbut-2-en-1-yl, 2-ethylbut-3-en-1-yl, 1,1,2-trimethylprop-2-en-1-yl, 1-ethyl-1-methylprop-2-en-1-yl, 1-ethyl-2-methylprop-1-en-1-yl, 1-ethyl-2-methylprop-2-en-1-yl, preferably ethenyl or prop-2-en-1-yl;

- C_2-C_4-alkynyl: ethynyl, prop-1-yn-1-yl, prop-2-yn-3-yl, n-but-1-yn-1-yl, n-but-1-yn-4-yl, n-but-2-yn-1-yl, preferably prop-2-yn-1-yl;

- C_1-C_2-haloalkyl: for example chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, preferably difluoromethyl or trifluoromethyl;

- C_1-C_6-haloalkyl: C_1-C_6-alkyl as mentioned above which is partially or fully substituted by fluorine, chlorine and/or bromine, i.e., for example, the abovementioned C_1-C_2-haloalkyl radicals, and also 3-chloropropyl or heptafluoropropyl,

preferably trifluoromethyl, pentafluoroethyl or heptafluoropropyl;

- C_2-C_6-haloalkenyl: C_2-C_6-alkenyl as mentioned above which is partially or fully substituted by fluorine, chlorine and/or bromine, i.e., for example, 2-chloroallyl, 3-chloroallyl or 3,3-dichloroallyl;

- C_2-C_4-haloalkynyl: C_2-C_4-alkynyl as mentioned above which is partially or fully substituted by fluorine, chlorine and/or bromine, for example chloroethynyl, 3-chloropropynyl;

- C_3-C_6-cycloalkyl: cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, preferably cyclopropyl, cylopentyl or cyclohexyl;

- halo-C_3-C_6-cycloalkyl: C_3-C_6-cycloalkyl as mentioned above which is partially or fully substituted by fluorine, chlorine and/or bromine, i.e., for example, 2-, 3- or 4-Chlorocyclopentyl, 2-, 3- or 4-chlorocyclohexyl, 2,3,4-trichlorocyclopentyl or 2,3,4,5,6-pentachlorocyclohexyl;

- aryl is preferably phenyl or naphthyl, in particular phenyl.

The unsaturated heterocycle having 5 or 6 ring atoms can be aromatic or nonaromatic. Aromatic heterocycles are, in particular, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,3,4-triazol-2-yl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, in particular furanyl, thienyl, oxazolyl and thiazolyl.

If the aryl radical is substituted, it has preferably one or two substituents which are independently of one another selected from the group consisting of halogen, in particular fluorine or chlorine, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, nitro, OH and CN. Preference is given to halogen and/or C_1-C_4-alkyl.

The substituents in the formula 1 preferably have the following meaning:

X is C_1-C_4-alkoxy or halogen, in particular C_1-C_4-alkoxy;

R_1 is H, C_1-C_4-alkyl, halogen, halo-C_1-C_4-alkyl, in particular H or C_1-C_4-alkyl;

R_2 is H, C_1-C_4-alkyl, halogen, halo-C_1-C_4-alkyl, in particular H or C_1-C_4-alkyl;

R_3 is C_1-C_4-alkyl;

R_5 is H or C_1-C_4-alkyl;

R_6 is H, C_1-C_4-alkyl or halo-C_1-C_4-alkyl, in particular H or C_1-C_4-alkyl;

R_7 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl or phenyl, in particular H, halogen, C_1-C_6-alkyl and particularly preferably H or halogen;

R_8 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, C_2-C_6-alkenyl or phenyl, in particular H, halogen, C_1-C_6-alkyl; or

R_7 and R_8, together with the carbon atoms to which they are attached, are a thienyl, furyl, oxazolyl or thiazolyl radical, where these groups may be substituted by C_1-C_4-alkyl, halogen or phenyl which may be substituted by one or two halogen, and are in particular thienyl or oxazolyl, where these groups may be substituted by one or two halogen or phenyl and the phenyl substituent for its part may be substituted by one or two halogen;

R_9 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl or phenyl, in particular H, halogen, C_1-C_6-alkyl and particularly preferably H or halogen;

R_{10} is H or C_1-C_4-alkyl.

The oxime side-chain may be attached to the phenyl ring in the o-, m- or p-position to W. Preference is given to the p-position.

The radical R_1 is preferably located in the 6-position.

If the oxime side-chain is attached in the p-position to W, the radical R_2 is preferably in the 2- and/or 5-position.

Preferred embodiments are the compounds of the formula 1 where:

A)

W is $-OCH_2-$, $-C(R_{10})=N-O-CH_2$;

X is halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy;

R_1 is H, C_1-C_4-alkyl, halogen, halo-C_1-C_4-alkyl;

R_2 is H, C_1-C_4-alkyl, halogen, halo-C_1-C_4-alkyl;

R_3 is H, C_1-C_4-alkyl;

n is 1 or 2;

R_5 is H or C_1-C_4-alkyl;

R_6 is H, C_1-C_4-alkyl, halo-C_1-C_4-alkyl;

R_7 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, phenyl;

R_8 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, C_2-C_6-alkenyl, phenyl; or

R_7 and R_8, together with the carbon atoms to which they are attached, form an unsaturated heterocycle having 5 or 6 ring atoms and one or two heteroatoms, independently of one another selected from nitrogen, oxygen and sulfur, which heterocycle may be substituted by one or two radicals which, independently of one another, are C_1-C_4-alkyl, halogen, halo-C_1-C_4-alkyl, C_1-C_4-alkoxy and phenyl which may be substituted by one or two halogen or C_1-C_4-alkyl;

R_9 is H, halogen, C_1-C_6-alkyl, halo-C_1-C_6-alkyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl, phenyl;

R_{10} is H, halogen, C_1-C_4-alkyl;

B)

W is $-OCH_2-$, $-C(R_{10})=N-O-CH_2$;

X is halogen, C_1-C_4-alkoxy;

R_1 is H, C_1-C_4-alkyl;

R_2 is H, C_1-C_4-alkyl;

n is 1 or 2;

R_3 is C_1-C_4-alkyl;

R_5 is H, C_1-C_4-alkyl;

R_6 is H, C_1-C_4-alkyl;

R_7 is H, halogen, C_1-C_6-alkyl;

R_8 is H, halogen, C_1-C_6-alkyl; or

R_7 and R_8, together with the carbon atoms to which they are attached, form a thienyl, furanyl, oxazolyl or thiazolyl radical, where these groups may have one or two substituents which are selected independently of one another from the group consisting of C_1-C_4-alkyl, halogen and phenyl which may be substituted by one or two halogen;

R_9 is H, halogen, C_1-C_6-alkyl;

R_{10} is H, C_1-C_4-alkyl;

C)

W is $-OCH_2-$, $-C(R_{10})=N-O-CH_2$;

X is C_1-C_4-alkoxy;

R_1 is H;

R_2 is H, C_1-C_4-alkyl;

n is 1 or 2;

R_3 is C_1-C_4-alkyl;

R_5 is H, C_1-C_4-alkyl;

R_6 is H, C_1-C_4-alkyl;

R_7 is H, halogen;

R_8 is H, C_1-C_4-alkyl, halogen; or

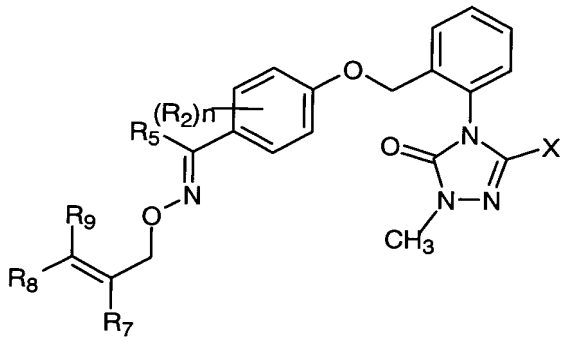
R_7 and R_8, together with the carbon atoms to which they are attached, form a thiophenyl or oxazolyl radical, where these groups may be substituted by one or two halogen or phenyl and the phenyl may be substituted by one or two halogen;

R_9 is H, halogen;

R_{10} is H, C_1-C_4-alkyl;

Further embodiments are

D) compounds of the formula 1a:



1a

where

X is chlorine, methoxy;

R_2 is chlorine, methyl;

n is 1 or 2, where R_2 is in the 2-position to the oxygen substituent if n = 1 and in the 2,5-position if n = 2;

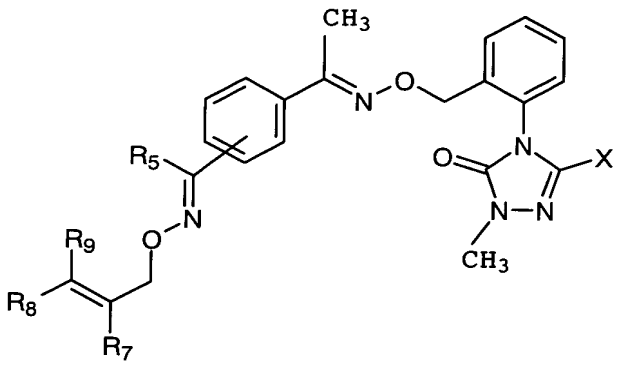
R_5 is H, methyl, ethyl;

R_7 is H, methyl, chlorine;

R_8 is H, methyl, ethyl, chlorine, phenyl, ethenyl, prop-1-en-1-yl;

R_9 is H, methyl, chlorine;

E) compounds of the formula 1b:



1b

where:

X is chlorine, methoxy;

R_5 is H, methyl, ethyl;

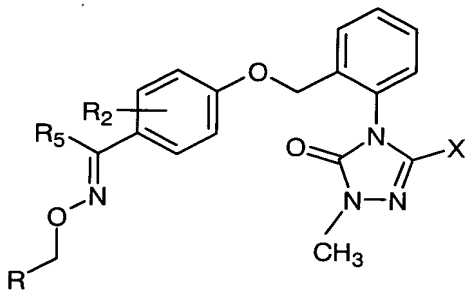
R_7 is H, methyl, chlorine;

R_8 is H, methyl, ethyl, chlorine, phenyl, ethenyl, prop-1-en-1-yl;

R_9 is H, methyl, chlorine.

The oxime side-chain is preferably attached in the p-position.

F) Compounds of the formula 1c:



1c

in which R is:

thiophen-2-yl, thiophen-3-yl, furan-2-yl, furan-3-yl, 5-chlorothiophen-2-yl, 5-bromothiophen-2-yl, 5-chlorofuran-2-yl, 5-bromofuran-2-yl, 5-methylthiophen-2-yl, 5-phenylthiophen-2-yl, 5-methylfuran-2-yl, 5-phenylfuran-2-yl, oxazol-4-yl, oxazol-5-yl, 2-(p-chlorophenyl)oxazol-4-yl, 2-(p-bromophenyl)oxazol-4-yl, thiazol-4-yl, thiazol-5-yl.

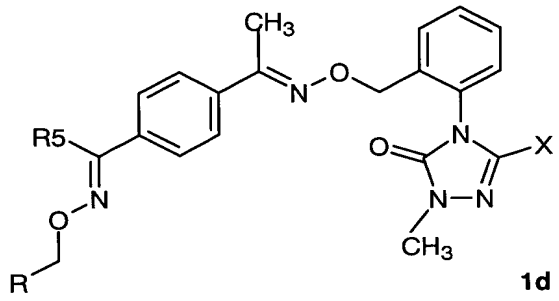
Here, the radicals X, R_2 and R_5 have the meanings mentioned above or, preferably, the following meanings:

X is chlorine, methoxy;

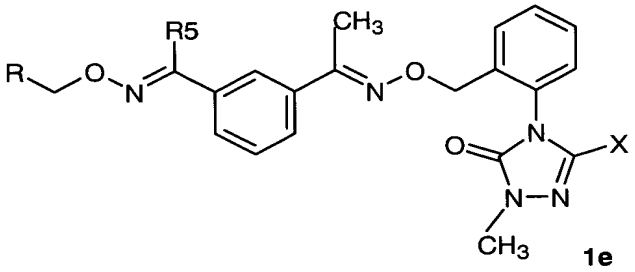
R_2 is 2-methyl, 2-chloro, 2,5-dimethyl;

R_5 is H, methyl, ethyl.

G) Compounds of the formulae 1d, 1e and 1f:



1d



1e

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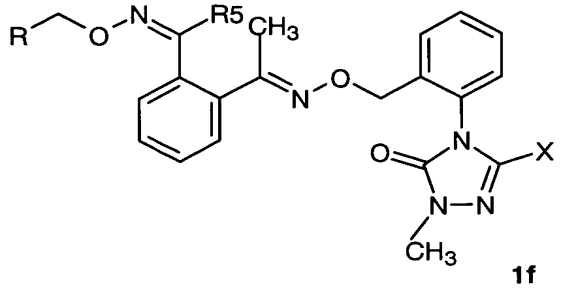


1f

in which R is:

thiophen-2-yl, thiophen-3-yl, furan-2-yl, furan-3-yl, 5-chlorothiophen-2-yl, 5-bromothiophen-2-yl, 5-chlorofuran-2-yl, 5-bromofuran-2-yl, 5-methylthiophen-2-yl, 5-phenylthiophen-2-yl, 5-methylfuran-2-yl, 5-phenylfuran-2-yl, oxazol-4-yl, oxazol-5-yl, 2-(p-chlorophenyl)oxazol-4-yl, 2-(p-bromophenyl)oxazol-4-yl, thiazol-4-yl, thiazol-5-yl.

Here, the radicals X and R_5 have the meanings given above or, preferably, the following meanings:

X is chlorine, methoxy;

R_5 is H, methyl, ethyl.

In particular with respect to their use, preference is given to the compounds of the formulae 1c to 1f compiled below. The groups mentioned here for a substituent are furthermore on their own, independently of the combination in which they are mentioned, a particularly preferred embodiment of the respective substituent:

a) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

b) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

c) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

d) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

e) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

f) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

g) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

h) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

i) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

j) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

k) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

l) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

m) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

n) Compounds of the formula 1c in which R_2 is 2-methyl (based on the oxygen substituent), X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

o) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

p) Compounds of the formula 1c in which R_2 is 2-chloro (based on the oxygen substituent), X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

q) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

r) Compounds of the formula 1c in which R_2 is 2,5-dimethyl (based on the oxygen substituent), X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

s) Compounds of the formula 1d in which X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

t) Compounds of the formula 1d in which X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

u) Compounds of the formula 1d in which X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

v) Compounds of the formula 1d in which X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

w) Compounds of the formula 1d in which X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

x) Compounds of the formula 1d in which X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

y) Compounds of the formula 1e in which X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

z) Compounds of the formula 1e in which X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

aa) Compounds of the formula 1e in which X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

ab) Compounds of the formula 1e in which X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

ac) Compounds of the formula 1e in which X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

ad) Compounds of the formula 1e in which X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

ae) Compounds of the formula 1f in which X is chlorine and R_5 is hydrogen and R corresponds to a row of Table 1.

af) Compounds of the formula 1f in which X is methoxy and R_5 is hydrogen and R corresponds to a row of Table 1.

ag) Compounds of the formula 1f in which X is chlorine and R_5 is methyl and R corresponds to a row of Table 1.

ah) Compounds of the formula 1f in which X is methoxy and R_5 is methyl and R corresponds to a row of Table 1.

ai) Compounds of the formula 1f in which X is chlorine and R_5 is ethyl and R corresponds to a row of Table 1.

aj) Compounds of the formula 1f in which X is methoxy and R_5 is ethyl and R corresponds to a row of Table 1.

Table 1

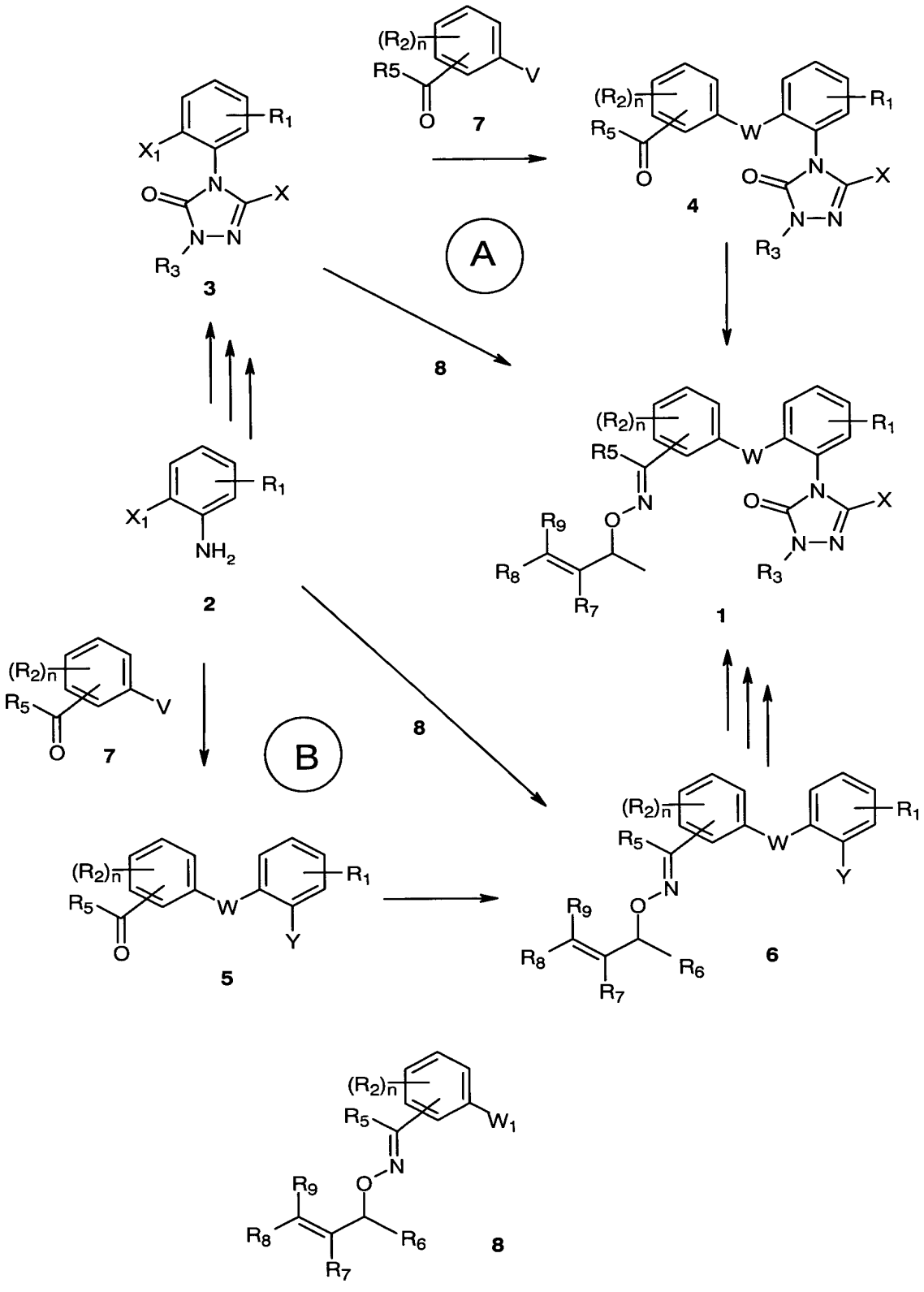
(E), (E,E) and (Z) refer to the substituents on the double bond indicated in R.

Number	R
1.	$-CH=CH_2$
2.	(E) $-CH=CH-CH_3$
3.	(Z) $-CH=CH-CH_3$
4.	$-CH=C(CH_3)_2$
5.	(E) $-CH=CH-C_2H_5$
6.	(Z) $-CH=CH-C_2H_5$
7.	(E) $-CH=C(CH_3)-C_2H_5$
8.	(Z) $-CH=C(CH_3)-C_2H_5$
9.	$-CH=C(C_2H_5)_2$
10.	(E) $-CH=CH-Cl$
11.	(Z) $-CH=CH-Cl_3$
12.	(E) $-CH=C(Cl)-CH$
13.	(Z) $-CH=C(Cl)-CH_3$
14.	(E) $-CH=C(Cl)-C_2H_5$
15.	(Z) $-CH=C(Cl)-C_2H_5$
16.	$-CH=CCl_2$
17.	(E) $-CH=CH-CH=CH_2$
18.	(E,E) $-CH=CH-CH=CH-CH_3$
19.	(E,E) $-CH=CH-CH=CH-C_6H_5$
20.	(E,E) $-CH=CH-CH=CH-(p-F-C_6H_4)$
21.	(E,E) $-CH=CH-CH=CH-(p-Cl-C_6H_4)$
22.	$-C(CH_3)=CH_2$

23.	(E) $-C(CH_3)=CH-CH_3$
24.	(Z) $-C(CH_3)=CH-CH_3$
25.	$-C(CH_3)=C(CH_3)_2$
26.	(E) $-C(CH_3)=CH-C_2H_5$
27.	(Z) $-C(CH_3)=CH-C_2H_5$
28.	(E) $-C(CH_3)=C(CH_3)-C_2H_5$
29.	(Z) $-C(CH_3)=C(CH_3)-C_2H_5$
30.	$-C(CH_3)=C(C_2H_5)_2$
31.	(E) $-C(CH_3)=CH-Cl$
32.	(Z) $-C(CH_3)=CH-Cl$
33.	(E) $-C(CH_3)=C(Cl)-CH_3$
34.	(Z) $-C(CH_3)=C(Cl)-CH_3$
35.	(E) $-C(CH_3)=C(Cl)-C_2H_5$
36.	(Z) $-C(CH_3)=C(Cl)-C_2H_5$
37.	$-C(CH_3)=CCl_2$
38.	(E) $-C(CH_3)=CH-CH=CH_2$
39.	(E,E) $-C(CH_3)=CH-CH=CH-CH_3$
40.	(E,E) $-C(CH_3)=CH-CH=CH-C_6H_5$
41.	(E,E) $-C(CH_3)=CH-CH=CH-(p\text{-}F\text{-}C_6H_4)$
42.	(E,E) $-C(CH_3)=CH-CH=CH-(p\text{-}Cl\text{-}C_6H_4)$
43.	$-C(C_2H_5)=CH_2$
44.	(E) $-C(C_2H_5)=CH-CH_3$
45.	(Z) $-C(C_2H_5)=CH-CH_3$
46.	$-C(C_2H_5)=C(CH_3)_2$
47.	(E) $-C(C_2H_5)=CH-C_2H_5$
48.	(Z) $-C(C_2H_5)=CH-C_2H_5$
49.	(E) $-C(C_2H_5)=C(CH_3)-C_2H_5$
50.	(Z) $-C(C_2H_5)=C(CH_3)-C_2H_5$
51.	$-C(C_2H_5)=C(C_2H_5)_2$
52.	(E) $-C(C_2H_5)=CH-Cl$
53.	(Z) $-C(C_2H_5)=CH-Cl$
54.	(E) $-C(C_2H_5)=C(Cl)-CH_3$
55.	(Z) $-C(C_2H_5)=C(Cl)-CH_3$
56.	(E) $-C(C_2H_5)=C(Cl)-C_2H_5$
57.	(Z) $-C(C_2H_5)=C(Cl)-C_2H_5$
58.	$-C(C_2H_5)=CCl_2$
59.	(E) $-C(C_2H_5)=CH-CH=CH_2$
60.	(E,E) $-C(C_2H_5)=CH-CH=CH-CH_3$
61.	(E,E) $-C(C_2H_5)=CH-CH=CH-C_6H_5$
62.	(E,E) $-C(C_2H_5)=CH-CH=CH-(p\text{-}F\text{-}C_6H_4)$
63.	(E,E) $-C(C_2H_5)=CH-CH=CH-(p\text{-}Cl\text{-}C_6H_4)$
64.	thiophen-2-yl
65.	thiophen-3-yl
66.	furan-2-yl
67.	furan-3-yl
68.	5-chlorothiophen-2-yl
69.	5-bromothiophen-2-yl
70.	5-chlorofuran-2-yl
71.	5-bromofuran-2-yl
72.	5-methylthiophen-2-yl
73.	5-phenylthiophen-2-yl
74.	5-methylfuran-2-yl

75.	5-phenylfuran-2-yl
76.	oxazol-4-yl
77.	oxazol-5-yl
78.	thiazol-4-yl
79.	thiazol-5-yl
80.	2-phenyloxazol-4-yl
81.	2-phenylthiazol-4-yl
82.	2-(p-chlorophenyl)oxazol-4-yl
83.	2-(p-chlorophenyl)thiazol-4-yl
84.	2-(p-bromophenyl)oxazol-4-yl
85.	2-(p-bromophenyl)thiazol-4-yl
86.	2-(p-fluorophenyl)oxazol-4-yl
87.	2-(p-fluorophenyl)thiazol-4-yl
88.	2-(2,4-dichlorophenyl)oxazol-4-yl
89.	2-(2,4-dichlorophenyl)thiazol-4-yl

The compounds according to the invention can be prepared by a plurality of methods. The preparation is preferably carried out by one of the synthesis routes A or B which are illustrated in the formula scheme below. The synthesis starts with a compound of the formula 2 in which X_1 in the case of route A is CH_3 or $PGOCH_2$-, where PG is a protective group for benzyl ethers. After the synthesis of the triazolone ring, the protective group is cleaved off and the resulting benzyl alcohol is converted by methods known from the literature into X_2CH_2-, X_2 being a nucleophilically removable group (cf. T. W. Greene: "Protective Groups in Organic Synthesis", 2nd Edition 1991, John Wiley, New York). In the case of route B, $X_1 = X_2CH_2$-, where X_2 is a nucleophilically removable group, such as, for example, chlorine, fluorine, bromine, nitro, alkyl- or arylsulfonate, such as mesylate, tosylate or triflate. The preparation of these compounds is known and, for example for the synthesis from the corresponding nitro compounds, described in Houben-Weyl, Vol. IV/1c, 4th Edition, p. 506ff, Thieme Verlag, Stuttgart 1980.


(R2)n
R5
V
7
R1
X1
N
O
X
N–N
R3
3
A
4
W
Y
8
2
NH2
B
5
6
R9
R8
R7
R6
1
W1

The amino function of the compounds 2 is initially converted into a thiazolone group, giving the compounds 3. The reaction sequence which leads to this conversion is described in detail in WO 95/14009 (compounds Nos. 21 → 19 → 17 → 1), and also in WO 96/26191 and DE 198 09 995.

The group X_1 is subsequently converted into a reactive group which can react with the radical V in the compound 7 or the radical W_1 in the compound of the formula 8, linking the two phenyl rings and forming the group W. The group V is a phenolic OH group or the group $C(R_{10})$=N-OH. Thus, a leaving group is introduced into the group X_1 and removed with the hydrogen atom of the phenolic or oximic OH group in the presence of a base. Examples of such leaving groups are chloride, bromide, p-toluenesulfonate, methanesulfonate or trifluoromethanesulfonate. These leaving groups are introduced in a manner known to the person skilled in the art, for example by reacting the compound 3 where X_1 = CH_3 with N-bromosuccinimide or N-chlorosuccinimide.

The reaction of the compound 3 with the compound 7 or 8 is carried out, for example, in an inert solvent or diluent, such as acetone, acetonitrile, dimethyl sulfoxide, dimethylformamide, N-methylpyrrolidone, etc., using a base (for example sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium hydride, potassium hydride, etc.). The bases are generally used in equimolar amounts or in excess. Moreover, it may be advantageous to add a catalytic amount of a crown ether (for example 18-crown-6 or 15-crown-5). The reaction temperature is generally in a range of from 0 to 80°C, preferably from 20 to 60°C.

The preparation of the compounds 7 and 8 is known to the person skilled in the art and described, for example, in Organikum, 17th Edition, VEB Deutscher Verlag der Wissenschaften, Berlin 1988, p. 323ff, and Angewandte Chemie, 84 (1972) 295, and also Zh. Org. Khim 31 (1995) 601, Chem. Pharm. Bull. 36 (1988) 3134, Indian J. Chem., Sect. B, 31 (1992), 495.

The compound 4, obtained by reaction of 3 with 7, is subsequently oxamated using an O-alkenylhydroxylamine or a salt thereof. The preparation of the O-alkenylhydroxylamine is known to the person skilled in the art and described, for example, in Chem. Pharm. Bull. 91 (1983), 2601 and J. Am. Chem. Soc. 71 (1949), 3423.

Alternatively, it is possible to react a compound 3 directly with an oxime 8 to give a compound 1. All steps of route A, including the preparation of the intermediates or analogous intermediates, are described in EP 386 581A (for W = OCH_2) and in EP 585 751A (for W = $C(R_{10})=NOCH_2$).

The starting material used for route B is likewise a compound 2. Reaction with the oxime 8 under the abovementioned etherification conditions gives a compound 6 (Y = NH_2). The thiazoline ring is then synthesized in the same manner as in route A.

Alternatively, a compound 2 is reacted with a compound 7 under the abovementioned etherification conditions to give a compound 5. This is oximated in the same manner as in route A, using O-alkenylhydroxylamine or a salt thereof, giving the compound 6 into which, as already described, the thiazolone ring is then introduced.

Owing to the C=C or C=N double bonds, the compounds according to the invention can be obtained in the preparation as E/Z isomer mixtures. These can be separated into the individual components in a customary manner, for example by crystallization or chromatography. Both the individual isomer compounds and their mixtures, and all enantiomers, racemates and diastereomers are embraced by the invention.

The novel compounds 1 have excellent activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the Ascomycetes and Basidiomycetes, and they can be employed as foliar- and soil-acting fungicides. Some of them have remarkably high systemic mobility and activity after soil application and in particular also after foliar application.

They are especially important for controlling a large number of fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, cotton, soybeans, coffee, sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, and cucurbits, and on the seeds of these plants.

Specifically, they are suitable for controlling the following plant diseases:
Erysiphe graminis (powdery mildew) in cereals,
Erysiphe cichoracearum and Sphaerotheca fuliginea on cucurbits,
Podosphaera leucotricha on apples,
Uncinula necator on grapevines,

Puccinia species on cereals,
Rhizoctonia species on cotton and lawns,
Ustilago species on cereals and sugar cane,
Venturia inaequalis (scab) on apples,
Helminthosporium species on cereals,
Septoria nodorum on wheat,
Botrytis cinerea (gray mold) on strawberries, grapevines,
Cercospora arachidicola on peanuts,
Pseudocercosporella herpotrichoides on wheat, barley,
Pyricularia oryzae on rice,
Phytophthora infestans on potatoes and tomatoes,
Fusarium and Verticillium species on a variety of plants,
Plasmopara viticola on grapevines,
Alternaria species on vegetables and fruit.

The compounds 1 are applied by treating the fungi, or the plants, seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application is effected before or after infection of the materials, plants or seeds by the fungi.

They can be converted into the customary formulations, such as solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the specific intended use; in any case, it should ensure fine and uniform distribution of the compounds 1 according to the invention. The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible to use other organic solvents as auxiliary solvents if water is used as the diluent. Suitable auxiliaries for this purpose are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. finely divided silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants such as lignin-sulfite waste liquors and methylcellulose.

The fungicidal compositions generally comprise from 0.1 to 95, preferably from 0.5 to 90, % by weight of active ingredient.

Depending on the nature of the desired effect, the rates of application are from 0.01 to 3 kg of active ingredient per ha.

In the treatment of seed, amounts of active ingredient of from 0.001 to 50 g, preferably 0.01 to 10 g, are generally required per kilogram of seed.

In the use form as fungicides, the compositions according to the invention can also exist together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides, or else with fertilizers.

A mixture with fungicides frequently results in a widened fungicidal activity spectrum.

The compounds of the formula 1a are furthermore suitable for effectively controlling pests from the class of the insects, arachnids and nematodes. They can be employed as pesticides in crop protection and in the hygiene, stored-product and veterinary sector.

The harmful insects include, from the order of the lepidopterans (Lepidoptera), for example, Agrotis ypsilon, Agrotis segetum, Alabama argillacea, Anticarsia gemmatalis, Argyresthia conjugella, Autographa gamma, Bupalus piniarius, Cacoecia murinana, Capua reticulana, Cheimatobia brumata, Choristoneura fumiferana, Choristoneura occidentalis, Cirphis unipuncta, Cydia pomonella, Dendrolimus pini, Diaphania nitidalis, Diatraea grandiosella, Earias insulana, Elasmopalpus lignosellus, Eupoecilia ambiguella, Evetria bouliana, Feltia subterranea, Galleria mellonella, Grapholitha funebrana, Grapholitha molesta, Heliothis armigera, Heliothis virescens, Heliothis zea, Hellula undalis, Hibernia defoliaria, Hyphantria cunea, Hyponomeuta malinellus, Keiferia lycopersicella, Lambdina fiscellaria, Laphygma exigua, Leucoptera coffeella, Leucoptera scitella, Lithocolletis blancardella, Lobesia botrana, Loxostege sticticalis, Lymantria dispar, Lymantria monacha, Lyonetia clerkella, Malacosoma neustria, Mamestra brassicae, Orgyia pseudotsugata, Ostrinia nubilalis, Panolis flammea, Pectinophora gossypiella, Peridroma saucia, Phalera bucephala, Phthorimaea operculella, Phyllocnistis citrella, Pieris brassicae, Plathypena scabra, Plutella xylostella, Pseudoplusia includens, Rhyacionia frustrana, Scrobipalpula absoluta, Sitotroga cerealella, Sparganothis pilleriana, Spodoptera frugiperda, Spodoptera littoralis, Spodoptera litura, Thaumatopoea pityocampa, Tortrix viridana, Trichoplusia ni, Zeiraphera canadensis.

From the order of the beetles (Coleoptera), for example, Agrilus sinuatus, Agriotes lineatus, Agriotes obscurus, Amphimallus solstitialis, Anisandrus dispar, Anthonomus grandis, Anthonomus pomorum, Atomaria linearis, Blastophagus piniperda, Blitophaga undata, Bruchus rufimanus, Bruchus pisorum, Bruchus lentis, Byctiscus betulae, Cassida nebulosa, Cerotoma trifurcata, Ceuthorrhynchus assimilis, Ceuthorrhynchus napi, Chaetocnema tibialis, Conoderus vespertinus, Crioceris asparagi, Diabrotica longicornis, Diabrotica 12-punctata, Diabrotica virgifera, Epilachna varivestis, Epitrix hirtipennis, Eutinobothrus brasiliensis, Hylobius abietis, Hypera brunneipennis, Hypera postica, Ips typographus, Lema bilineata, Lema melanopus, Leptinotarsa decemlineata, Limonius californicus, Lissorhoptrus oryzophilus, Melanotus communis, Meligethes aeneus, Melolontha hippocastani, Melolontha melolontha, Oulema oryzae, Otiorrhynchus sulcatus, Otiorrhynchus ovatus, Phaedon cochleariae, Phyllotreta chrysocephala, Phyllophaga sp., Phyllopertha horticola, Phyllotreta nemorum, Phyllotreta striolata, Popillia japonica, Sitona lineatus, Sitophilus granaria.

From the order of the dipterans (Diptera), for example, Aedes aegypti, Aedes vexans, Anastrepha ludens, Anopheles maculipennis, Ceratitis capitata, Chrysomya bezziana, Chrysomya hominivorax, Chrysomya macellaria, Contarinia sorghicola, Cordylobia anthropophaga, Culex pipiens, Dacus cucurbitae, Dacus oleae, Dasineura brassicae, Fannia canicularis, Gasterophilus intestinalis, Glossina morsitans, Haematobia irritans, Haplodiplosis equestris, Hylemyia platura, Hypoderma lineata, Liriomyza sativae, Liriomyza trifolii, Lucilia cuprina, Lucilia sericata, Lycoria pectoralis, Mayetiola destructor, Musca domestica, Muscina stabulans, Oestrus ovis, Oscinella frit, Pegomya hyoscyami, Phorbia antiqua, Phorbia brassicae, Phorbia coarctata, Rhagoletis cerasi, Rhagoletis pomonella, Tabanus bovinus, Tipula oleracea, Tipula paludosa.

From the order of the thrips (Thysanoptera), for example, Frankliniella fusca, Frankliniella occidentalis, Frankliniella tritici, Scirtothrips citri, Thrips oryzae, Thrips palmi, Thrips tabaci.

From the order of the hymenopterans (Hymenoptera), for example, Athalia rosae, Atta cephalotes, Atta sexdens, Atta texana, Hoplocampa minuta, Hoplocampa testudinea, Monomorium pharaonis, Solenopsis geminata, Solenopsis invicta.

From the order of the heteropterans (Heteroptera), for example, Acrosternum hilare, Blissus leucopterus, Cyrtopeltis notatus, Dysdercus cingulatus, Dysdercus intermedius, Eurygaster integriceps, Euschistus impictiventris, Leptoglossus phyllopus, Lygus lineolaris, Lygus pratensis, Nezara viridula, Piesma quadrata, Solubea insularis, Thyanta perditor.

From the order of the homopterans (Homoptera), for example, Acyrthosiphon onobrychis, Adelges laricis, Aphidula nasturtii, Aphis fabae, Aphis pomi, Aphis sambuci, Bemisia tabici, Brachycaudus cardui, Brevicoryne brassicae, Cerosipha gossypii, Dreyfusia nordmannianae, Dreyfusia piceae, Dysaphis radicola, Dysaulacorthum pseudosolani, Empoasca fabae, Macrosiphum avenae, Macrosiphum euphorbiae, Macrosiphon rosae, Megoura viciae, Metopolophium dirhodum, Myzodes persicae, Myzus cerasi, Nephotettix cincticeps, Nilaparvata lugens, Pemphigus bursarius, Perkinsiella saccharicida, Phorodon humuli, Psylla mali, Psylla piri, Rhopalomyzus ascalonicus, Rhopalosiphum maidis, Sappahis mali, Schizaphis graminum, Schizoneura lanuginosa, Trialeurodes vaporariorum, Viteus vitifolii.

From the order of the termites (Isoptera), for example, Calotermes flavicollis, Leucotermes flavipes, Reticulitermes lucifugus, Termes natalensis.

From the order of the orthopterans (Orthoptera), for example, Acheta domestica, Blatta orientalis, Blattella germanica, Forficula auricularia, Gryllotalpa gryllotalpa, Locusta migratoria, Melanoplus bivittatus, Melanoplus femur-rubrum, Melanoplus mexicanus, Melanoplus sanguinipes, Melanoplus spretus, Nomadacris septemfasciata, Periplaneta americana, Schistocerca americana, Schistocerca peregrina, Stauronotus maroccanus, Tachycines asynamorus.

From the class of the Arachnoidea, for example, arachnids (Acarina) such as Amblyomma americanum, Amblyomma variegatum, Argas persicus, Boophilus annulatus, Boophilus decoloratus, Boophilus microplus, Brevipalpus phoenicis, Bryobia praetiosa, Dermacentor silvarum, Eotetranychus carpini, Eriophyes sheldoni, Hyalomma truncatum, Ixodes ricinus, Ixodes rubicundus, Metatetranychus(Phanonychus)ulmi, Ornithodorus moubata, Otobius megnini, Paratetranychus pilosus, Dermanyssus gallinae, Phyllocoptruta oleivora, Polyphagotarsonemus latus, Psoroptes ovis, Rhipicephalus appendiculatus, Rhipicephalus evertsi, Sarcoptes scabiei, Tetranychus cinnabarinus, Tetranychus

kanzawai, Tetranychus pacificus, Tetranychus telarius, Tetranychus urticae.

From the class of the nematodes, for example, root knot nematodes, e.g. Meloidogyne hapla, Meloidogyne incognita, Meloidogyne javanica, cyst-forming nematodes, e.g. Globodera rostochiensis, Heterodera avenae, Heterodera glycines, Heterodera schachtii, Heterodera trifolii, stem eelworms and foliar nematodes, e.g. Belonolaimus longicaudatus, Ditylenchus destructor, Ditylenchus dipsaci, Heliocotylenchus multicinctus, Longidorus elongatus, Radopholus similis, Rotylenchus robustus, Trichodorus primitivus, Tylenchorhynchus claytoni, Tylenchorhynchus dubius, Pratylenchus neglectus, Pratylenchus penetrans, Pratylenchus curvitatus, Pratylenchus goodeyi.

The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of ready-to-spray solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; in any case, they should guarantee the finest possible distribution of the active ingredients according to the invention.

The concentrations of active ingredient in the ready-to-use preparations can be varied within substantial ranges.

In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active ingredients can also be used successfully in the ultra-low-volume method (ULV), it being possible to apply formulations with over 95% by weight of active ingredient, or even the active ingredient without additives.

Under field conditions, the rate of application of active ingredient for controlling pests is 0.1 to 2.0, preferably 0.2 to 1.0 kg/ha.

Substances which are suitable for the preparation of ready-to-spray solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point such as kerosene or diesel oil, furthermore coal-tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their

derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of wetting agent, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active ingredient, wetting agent, tackifier, dispersant or emulsifier and, if desired, solvent or oil, which are suitable for dilution with water.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

Examples of the formulations are:

Granules, e.g. coated granules, impregnated granules and homogeneous granules; they can be prepared by binding the active ingredients onto solid carriers. Examples of solid carriers are

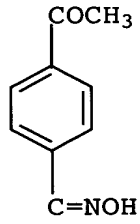
mineral earths such as silica gel, silicas, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin such as cereal meal, tree bark meal, wood meal and nut shell meal, cellulose powders, and other solid carriers.

Various types of oils, or herbicides, fungicides, other pesticides, or bactericides, can be added to the active ingredients, if appropriate also only just prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

In these use forms, the compositions according to the invention can also be present together with other active compounds, such as herbicides, insecticides, growth regulators and fungicides, or else be mixed and applied together with fertilizers. A mixture with fungicides frequently results in a widened fungicidal activity spectrum.

Example 1

Synthesis of 1,4-diacetylbenzene monooxime **9**

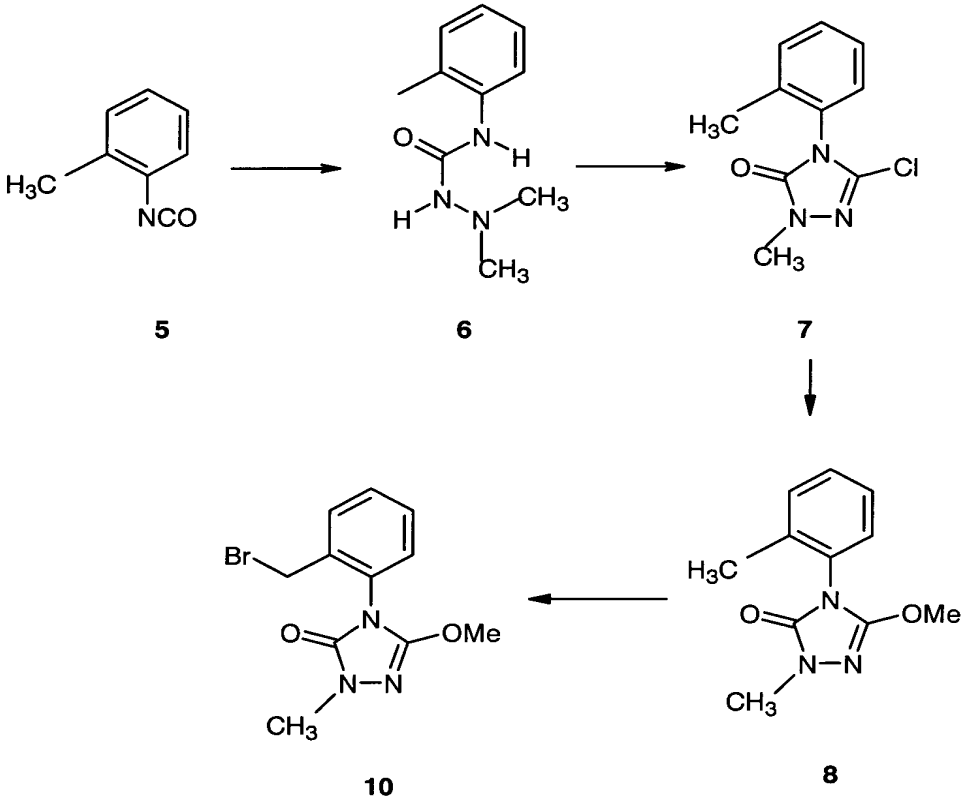


9

25 g (0.154 mol) of 1,4-diacetylbenzene and 12.2 g (0.154 mol) of pyridine are dissolved in 80 ml of methanol. Under reflux, a solution of 10.7 g (0.154 mol) of hydroxylammonium chloride in 50 ml of water is added slowly. The mixture is stirred under reflux for 6 h and then at room temperature for 15 h. The mixture is then filtered, and the residue is washed three times with water and dried under reduced pressure. This gives 24.7 g (90%) of the product as colorless crystals. Melting point: 162 - 169°C.

Example 2

Synthesis of **10**



5 **6** **7**

10 **8**

Synthesis of 1,1-dimethyl-4-(*ortho*-tolyl)semicarbazide **6**:

At 10-15°C, 23.7 g (0.395 mol) of 1,1-dimethylhydrazine are slowly added to a solution of 50 g (0.376 mol) of *ortho*-tolyl isocyanate in 400 ml of absolute toluene. The mixture is stirred at room temperature for 16 h and then concentrated under reduced pressure, and the residue is suspended in 100 ml of cyclohexane. Filtration and washing of the residue with pentane gives 69.2 g (95%) of the product in the form of colorless crystals. M.p.: 134 - 136°C.

Synthesis of 5-chloro-2,4-dihydro-2-methyl-4-(*ortho*-tolyl)-*3H*-1,2,4-triazol-3-one **7**:

At 0°C, 106 g (0.359 mol) of triphosgene (bis(trichloromethyl) carbonate) are added to a solution of 69.2 g (0.358 mol) of 1,1-dimethyl-4-(*ortho*-tolyl)semicarbazide **6**. The reaction mixture is stirred at room temperature for 72 h and then concentrated under reduced pressure, and the residue is taken up in 150 ml of ethyl acetate. Cooling to 0°C results in 39.2 g of product precipitating out. The mother liquor is concentrated under

reduced pressure and taken up in 1.5 l of ethyl acetate. The mixture is washed three times with water, dried over sodium sulfate and concentrated under reduced pressure, giving a total of 49.5 g (65%) of product in the form of a colorless powder. *400 MHz-^{1}H-NMR ($CDCl_3$), δ [ppm]:* 2.21 (s, 3H, Ar-CH_3); 3.52 (s, 3H, N-CH_3); 7.13-7.44 (m, 4H, Ar-H).

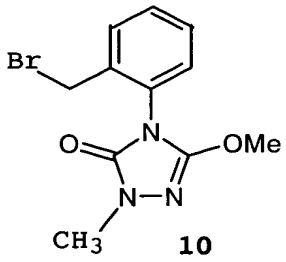
Synthesis of 2,4-dihydro-5-methoxy-2-methyl-4-(*ortho*-tolyl)-*3H*-1,2,4-triazol-3-one **8**:

79.2 g (0.44 mol) of a 30% strength sodium methoxide solution are added to a solution of 49.5 g (0.22 mol) of 5-chloro-2,4-dihydro-2-methyl-4-(*ortho*-tolyl)-*3H*-1,2,4-triazol-3-one **7** in 620 ml of a mixture of methanol and ethylene glycol dimethyl ether (1:1). The mixture is stirred under reflux for 6 h and then concentrated under reduced pressure, and the residue is taken up in ethyl acetate. The mixture is washed three times with water, dried over sodium sulfate and concentrated under reduced pressure. The crude product is taken up in 100 ml of MTBE, admixed with 150 ml of hexane and cooled to 0°C. The precipitate is separated off and dried at 40°C under reduced pressure for 1 h. This gives 37.6 g (78%) of the product as a pale beige powder. M.p.: 127 - 130 °C.

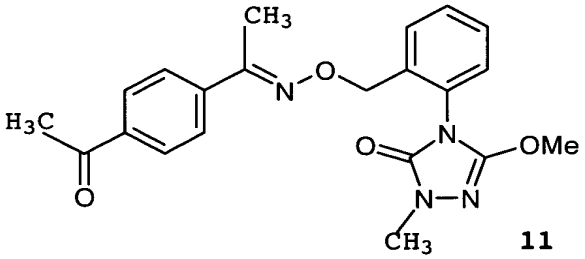
Synthesis of 4-(*ortho*-bromomethylenephenyl)-2,4-dihydro-5-methoxy-2-methyl-*3H*-1,2,4-triazol-3-one **10**:

A solution of 10.7 g (60 mmol) of *N*-bromosuccinimide in 150 ml of absolute 1,2-dichloroethane is added to a solution of 10.9 g (50 mmol) of 2,4-dihydro-5-methoxy-2-methyl-4-(*ortho*-tolyl)-*3H*-1,2,4-triazol-3-one **8** and 0.4 g of azobisisobutyronitrile in 150 ml of absolute 1,2-dichloroethane. For 1 h, the mixture is stirred under reflux and irradiated with UV light. The mixture is then washed three times with water, dried over sodium sulfate and concentrated under reduced pressure. Purification of the residue by flash chromatography gives 4.1 g (28%) of the product as a colorless powder. M.p.: 113 - 115 °C.

Example 3: Synthesis of **11**



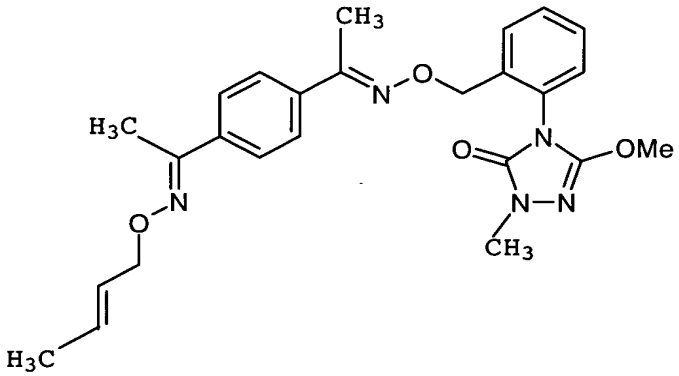
10



11

4.2 g (23 mmol) of 1,4-diacetylbenzene monooxime **9** are added to 0.62 g (26 mmol) of sodium hydride in 30 ml of absolute acetonitrile. The mixture is stirred under reflux for 1 h, and a solution of 7 g (23 mmol) of **10** in 50 ml of absolute acetonitrile is then added at room temperature. The reaction mixture is stirred at room temperature for 15 h and then taken up in dilute NaCl solution and extracted three times with methyl *tert*-butyl ether. The combined organic phase is washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue is purified by chromatography. This gives 7.2 g (79%) of the product as colorless crystals. Melting point 102 - 106°C.

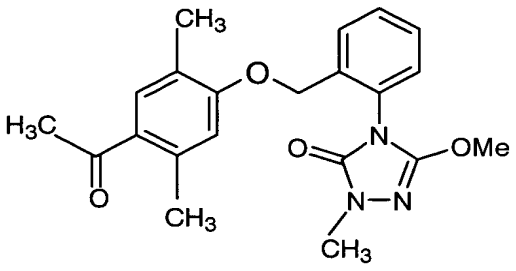
Example 4: Synthesis of **12**



12

0.44 g (3.6 mmol) of O-2-trans-butenehydroxylammonium chloride and 1 g of molecular sieve 3 Å are added to a solution of 1.1 g (2.8 mmol) of **11** in 40 ml of methanol. The mixture is stirred at room temperature for 15 h. The molecular sieve is filtered off and the reaction mixture is taken up in ethyl acetate, washed twice with water, dried with sodium sulfate and concentrated under reduced pressure. Chromatographic purification of the residue gives 840 ml (65%) of the residue as colorless crystals. Melting point 101 - 105°C.

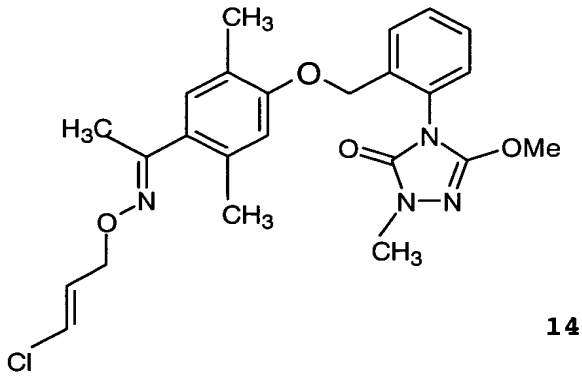
Example 5: Synthesis of **13**



13

1.33 g (55 mmol) of sodium hydride are added to a solution of 8.3 g (50 mmol) of 2,5-dimethyl-4-hydroxyacetophenone in 120 ml of absolute DMF (dimethylformamide). The mixture is stirred at room temperature for 1 h, and a solution of 15 g (50 mmol) of **10** in 80 ml of absolute DMF is then added, and the mixture is stirred at room temperature for 19 h. The mixture is then taken up in dilute NaCl solution and extracted three times with ethyl acetate. The combined organic phase is washed with water, dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification gives 13.9 g (73%) of the product.

Example 6: Synthesis of **14**

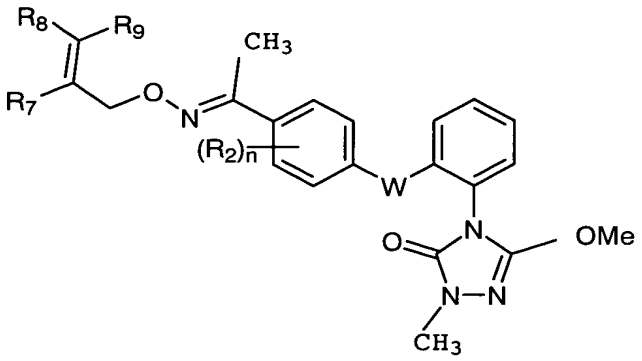


14

1 g (6 mmol) of **13** is dissolved in 40 ml of methanol. 0.42 g (2.9 mmol) of O-(3-chloroprop-2-ene)hydroxylammonium chloride and 1 g of molecular sieve 3 Å are added, and the mixture is stirred at room temperature for 15 h. The mixture is filtered and the filtrate is taken up in ethyl acetate, washed with water, dried with sodium sulfate and concentrated under reduced pressure, giving 1.1 g (89%) of the product (cf. Table No. 9 below).

The other compounds listed in Tables 2 and 3 below were obtained in a similar manner.

Table 2: Physical data of compounds of the formula:

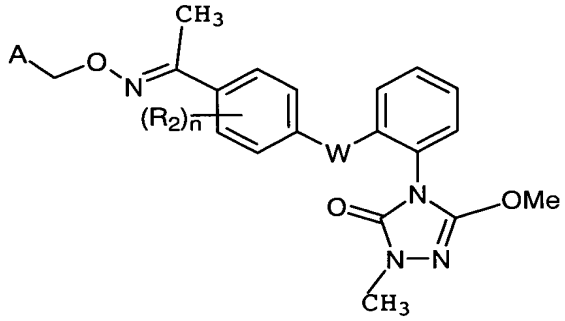


No.	n	W	R2	R7	R8	R9	Analyt. data
1	1	$-OCH_2-$	2-methyl	H	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.22 (s, 3H); 2.24 (s, 3H); 3.41 (s, 3H); 3.91 (s, 3H); 4.67 (d, 2H); 5.10 (s, 2H); 5.20-5.40 (m, 3H); 5.98-6.18 (m, 1H); 6.78 (d, 1H); 7.22-7.64 (m, 6H).
2	1	$-OCH_2-$	2-methyl	H	methyl	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 1.74 (d, 3H); 2.19 (s, 3H); 2.21 (s, 3H), 3.42 (s, 3H), 3.92 (s, 3H); 4.60 (d, 2H); 5.10 (s, 2H); 5.71-5.86 (m, 2H); 6.78 (d, 1H); 7.19-7.63 (m, 6H).
3	1	$-OCH_2-$	2-methyl	chloro	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.20 (s, 3H); 2.22 (s, 3H), 3.41 (s, 3H), 3.93 (s, 3H); 4.71 (s, 2H); 5.19 (s, 2H); 5.18 (s, 1H); 5.22 (s, 1H); 6.78 (d, 1H); 7.21-7.64 (m, 6H).
4		$-C(CH_3)=NOCH_2-$	H	H	chloro	H	M.p. = 112-117°C
5		$-C(CH_3)=NOCH_2-$	H	H	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.19 (s, 3H); 2.25 (s, 3H); 3.40 (s, 3H); 3.88 (s, 3H); 4.70 (d, 2H); 5.20-5.42 (m, 2H); 6.00-6.18 (m, 1H); 7.21-7.70 (m, 8H).
6		$-C(CH_3)=NOCH_2-$	H	H	methyl	H	M.p. = 101-105°C

7		$-C(CH_3)=NOCH_2-$	H	chloro	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.19 (s, 3H); 2.24 (s, 3H); 3.40 (s, 3H); 3.94 (s, 3H); 4.76 (s, 2H); 5.23 (d, 2H); 5.40 (s, 1H); 5.45 (s, 1H); 7.21-7.61 (m, 8H).
8	1	$-OCH_2-$	2-methyl	H	chloro	H	400MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.19 (s, 3H); 2.23 (s, 3H); 3.42 (s, 3H); 3.92 (s, 3H); 4.62 (d, 2H); 5.10 (d, 2H); 6.15 (m, 1H); 6.26 (d, 1H); 6.79 (d, 1H); 7.22-7.63 (m, 7H).
9	2	$-OCH_2-$	2,5-dimethyl	H	chloro	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.14 (s, 3H); 2.17 (s, 3H); 2.24 (s, 3H); 3.42 (s, 3H); 3.93 (s, 3H); 4.61 (s, 2H); 5.02 (s, 2H); 6.03-6.11 (m, 1H); 6.60 (s, 1H); 6.98-7.64 (m, 7H).
10	2	$-OCH_2-$	2,5-dimethyl	H	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.17 (s, 6H); 2.26 (s, 3H); 3.44 (s, 3H); 3.90 (s, 3H); 4.62 (s, 2H); 5.06 (s, 2H); 5.97-6.13 (m, 1H); 6.60 (s, 1H); 6.99 (s, 1H); 7.20-7.65 (m, 6H).
11	2	$-OCH_2-$	2,5-dimethyl	H	methyl	H	400MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 1.72 (d, 3H); 2.15 (s, 3H); 2.20 (s, 3H); 2.30 (s, 3H); 3.44 (s, 3H); 3.97 (s, 3H); 4.95 (d, 2H); 5.07 (s, 2H); 5.60-5.83 (m, 2H); 6.60-7.61 (m, 6H).
12	2	$-OCH_2-$	2,5-dimethyl	chloro	H	H	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.07 (s, 3H); 2.15 (s, 3H); 2.26 (s, 3H); 3.42 (s, 3H); 3.95 (s, 3H); 4.85 (s, 2H); 5.05 (s, 2H); 5.14-5.23 (m, 2H); 6.60 (s, 1H); 7.21-7.63 (m, 5H).

13	1	$-OCH_2-$	2-methyl	H	H	chloro	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.18 (s, 3H); 2.23 (s, 3H); 3.41 (s, 3H); 3.90 (s, 3H); 4.93 (d, 2H); 5.09 (s, 2H); 6.02-6.21 (m, 2H); 6.88 (d, 1H); 7.21-7.64 (m, 7H).
14	2	$-OCH_2-$	2,5-dimethyl	H	H	chloro	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.07 (s, 3H); 2.18 (s, 3H); 2.25 (s, 3H); 3,43 (s, 3H); 3.92 (s, 3H); 4.82 (d, 2H); 6.00-7.64 (m, 8H).

Table 3: Physical data of compounds of formula:



No.	n	W	R2	A	Analyt. data
15	1	$-OCH_2-$	2-methyl	5-chlorothiophen-2-yl	400MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.19 (s, 3H); 2.23 (s, 3H); 3.42 (s, 3H); 3.89 (s, 3H); 5.19-5.30 (m, 4H); 6.79 (s, 1H); 6.84 (s, 1H); 7.23-7.70 (m, 8H).
16	1	$-OCH_2-$	2-methyl	2-(para-bromophenyl)oxazol-4-yl	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 1.59 (s, 3H); 2.23 (s, 3H), 3.41 (s, 3H), 3.95 (s, 3H); 5.10 (s, 2H); 5.21 (s, 2H); 6.80-7.95 (m, 12H).
17	1	$-OCH_2-$	2-methyl	2-(para-chlorophenyl)oxazol-4-yl	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 1.60 (s, 3H); 2.21 (s, 3H), 3.41 (s, 3H), 3.90 (s, 3H); 5.09 (s, 2H); 5.19 (s, 2H); 6.80 (d, 1H); 7.21-8.02 (m, 11H).

18	1	$-OCH_2-$	2-methyl	thiophen-3-yl	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.20 (s, 3H); 2.24 (s, 3H), 3.42 (s, 3H), 3.94 (s, 3H); 4.81 (d, 2H); 5.12 (s, 2H); 6.20-6.38 (m, 1H); 6.61-6.80 (m, 2H); 7.15-7.64 (m, 10H).
19		$-C(CH_3)=NOCH_2-$	H	5-chlorothiophen-2-yl	M.p. = 106-114°C
20		$-C(CH_3)=NOCH_2-$	H	2-(para-bromophenyl)oxazol-4-yl	360MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.17 (s, 3H); 2.21 (s, 3H), 3.35 (s, 3H), 3.43 (s, 3H); 4.80 (d, 2H); 5.21 (s, 2H); 7.18-7.95 (m, 13H).
21		$-C(CH_3)=NOCH_2-$	H	thiophen-3-yl	M.p. = 109-126°C
22	2	$-OCH_2-$	2,5-dimethyl	5-chlorothiophen-2-yl	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.17 (s, 3H); 2.20 (s, 3H); 2.30 (s, 3H); 3.41 (s, 3H); 3.96 (s, 3H); 5.02 (s, 2H); 5.19 (s, 2H); 6.80-7.66 (m, 8H).
23	2	$-OCH_2-$	2,5-dimethyl	2-(para-bromophenyl)oxazol-4-yl	IR (cm^{-1}): 1725, 1616, 1501, 1479, 1414, 1402, 1389, 1325, 1247, 1149, 1073, 1037, 1010, 744, 733.
24	2	$-OCH_2-$	2,5-dimethyl	thiophen-3-yl	270MHz-^{1}H-NMR ($CDCl_3$), δ (ppm): 2.16 (s, 3H); 2.19 (s, 3H); 2.29 (s, 3H); 3.42 (s, 3H); 3.93 (s, 3H); 4.78 (d, 2H); 5.02 (s, 2H); 6.21-6.40 (m, 1H); 6.60-7.62 (m, 10H).
25	2	$-OCH_2-$	2,5-dimethyl	2-(para-chlorophenyl)oxazol-4-yl	M.p. = 92-117°C

Use Examples

Experiment 1 - Activity against mildew of wheat

Leaves of wheat seedlings c.v. "Frühgold" grown in pots were sprayed to runoff point with an aqueous preparation of active compound which had been prepared from a stock solution comprising 10% of active compound, 63% of cyclohexanone and 27% of emulsifier and, 24 hours after the spray coating had dried on, dusted with spores of mildew of wheat (Erysiphe graminis forma specialis tritici). The test plants were then placed in a greenhouse at 20-24°C and 60-90% relative atmospheric humidity.

After 7 days, the extent of the mildew development was determined visually in % infection of the total leaf area.

Active compound [1]	% Infection of the leaves after application of an aqueous preparation comprising 63 ppm of active compound
Active compound No. 1	5
Active compound No. 2	10
Active compound No. 3	5
Active compound No. 8	0
Active compound No. 9	3
Active compound No. 10	3
Active compound No. 11	0
Active compound No. 12	5
Active compound No. 13	10
Active compound No. 14	5
Active compound No. 15	15
Active compound No. 16	5
Active compound No. 17	10
Active compound No. 18	10
Active compound No. 22	5
Active compound No. 23	3
Active compound No. 24	5
Active compound No. 25	5
Untreated	90

[1] See Tables 2 and 3

Experiment 2 - Activity against Plasmopara viticola

Leaves of potted vines c.v. "Müller-Thurgau" were sprayed to runoff point with an aqueous preparation of active compound which had been prepared from a stock solution comprising 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. The next day, the leaves were inoculated with an aqueous zoospore suspension of Plasmopara viticola. The vines were then initially placed in a water-vapor-saturated chamber at 24°C for 48 hours and then in a greenhouse at 20-30°C for 5 days. After this time, the plants were once more placed in a humid chamber for 16 hours, to promote sporangiophore eruption. The extent of the development of the infection on the underside of the leaves was then determined visually.

Active compound [1]	% Infection of the leaves after application of an aqueous preparation comprising 63 ppm of active compound
Active compound No. 1	10
Active compound No. 2	10
Active compound No. 5	0
Active compound No. 7	10
Active compound No. 8	10
Active compound No. 9	1
Active compound No. 10	0
Active compound No. 11	0
Active compound No. 12	0
Active compound No. 13	15
Active compound No. 14	0
Active compound No. 25	15
Untreated	85

[1] See Tables 2 and 3

Experiment 3 - Activity against Pyricularia oryzae (protective)

Leaves of rice seedlings c.v. "Tai-Nong 67" grown in pots were sprayed to runoff point with an aqueous preparation of active compound which had been prepared from a stock solution comprising 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. The next day, the plants were inoculated with an aqueous sporangiophore suspension of Pyricularia oryzae. The test plants were then placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the infection on the leaves was then determined visually.

Active compound [1]	% Infection of the leaves after application of an aqueous preparation comprising 63 ppm of active compound
Active compound No. 4	15
Active compound No. 5	5
Active compound No. 6	10
Active compound No. 7	5
Active compound No. 8	5
Active compound No. 9	5
Active compound No. 11	10
Active compound No. 12	10

Active compound No. 13	5
Active compound No. 14	5
Active compound No. 15	10
Active compound No. 22	5
Active compound No. 23	5
Active compound No. 24	5
Active compound No. 25	5
Untreated	90

1) See Tables 2 and 3